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TRANSLATION FROM BULGARIAN!

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PATENT OFFICE

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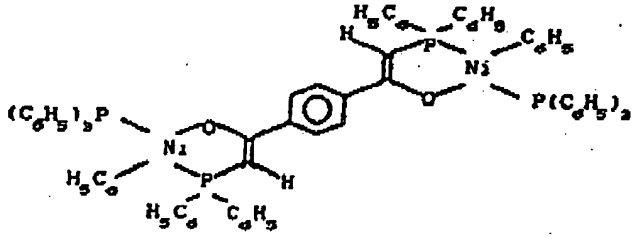
(54) CATALYST FOR POLYMERIZATION OF ETHYLENE AND A METHOD FOR ITS PRODUCING

(57) The catalyst according to the present invention is used for producing linear polyethylene in a medium of polar or non-polar solvents, or mixtures thereof, at temperature from 0 to 120°C, concentration of the catalyst from 5.10^{-3} mol/l to 1 mol/l, and pressure of ethylene from 1 to 150 atmospheres. The catalyst for polymerization of ethylene has the following formula



where R_1, R_2, R_3, R_6, R_7, and R_8 are independently alkyl groups containing 1 to 10 carbon atoms; aryl groups containing 6 to 10 carbon atoms; arylalkyl groups containing 7 to 20 carbon atoms; alkylaryl groups containing

7 to 20 carbon atoms; R_4 and R_5 are independently hydrogen, alkyl groups containing 1 to 10 carbon atoms. According to the method Ni (O) compounds react with bis-α-keto-ylides or with tertiary phosphines in a medium of polar or non-polar solvents, or mixtures thereof, at a temperature from -20°C to 80°C.

7 claims

(5(54) CATALYST FOR POLYMERIZATION OF ETHYLENE AND A METHOD FOR ITS PRODUCING

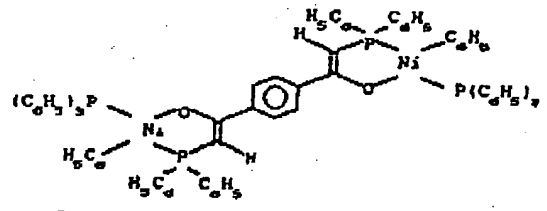
The present invention is related to a catalyst for polymerization of ethylene and a method for its producing.

It is known that nickel complexes containing chelated bound α-keto-ylide ligands, are active catalysts for oligomerization of ethylene to linear α-alkenes [1, 2]. Modification in situ of these organometallic compounds converts them into bicomponent catalysts for polymerization of ethylene to linear polyethylene [3]. For example, the use of α-keto-ylide nickel complexes modified with different phosphine acceptor additives as catalysts for polymerization of ethylene, is well-known [4]. Nickel-ylide complexes [5, 6] also catalyze polymerization of ethylene to linear polyethylene. These are bicomponent catalysts that are produced in situ during the catalytic process.

The disadvantages of the above-described catalysts for polymerization of ethylene are their not particularly high activity and the need for a second component.

The aim of the present invention is to provide a catalyst for polymerization of ethylene to linear polyethylene, acting without presence of modifying additives and having relatively high catalytic activity, and a method for its producing.

The aim is achieved by a catalyst for polymerization of ethylene of the following formula:



Also the aim of the invention is achieved by a method for producing a catalyst by reaction of Ni (O) compounds with bis-α-keto-ylides or with tertiary phosphines in a medium of polar or non-polar solvents, or mixtures thereof, at a temperature from -20°C to 80°C. Bis-1,5-cyclo-octa-di-ene nickel (O), bis-nor-borna-di-ene nickel (O), tetra-cis-triphenyl-phosphine nickel (O), tetra-cis-trinaphtyl-phosphine nickel (O), are used as Ni (O) compounds.

Advantages of the catalyst according to the present invention are its monocomponent structure and high activity compared to known nickel-ylide catalysts for polymerization of ethylene.

The following examples will illustrate the invention.

Example 1. To 1,71 g (2,5 mmol) of 1,4-[(1-triphenyl-phospho-anilideno)-acetyl]benzol 1,37 g (5 mmol) of triphenyl-phosphine, dissolved in 200 cm^3 benzol, is added at 0°C. The mixture is stirred for 24 hours at 50°C. After cooling to room temperature, 50 cm^3 n-hexane is added to the reaction mixture in an invert medium, through a glass fiter G-3. The formed precipitate is washed with 30 cm^3 mixture (1:1) of benzol and hexane and is dried under vacuum (0,1 torr) for 2 h at 50°C. Yield: 1,65 g (50 % of the theoretical products).

Analysis:

Elementary analysis:

Calculated: C – 74,35 % H – 4,99 %

Found: C – 73,93 % H – 4,79 %

IR-spectrum (cm^{-1}): 1560 (ν_{c-c}), 1523 (ν_{c-o}), 1478 ($\nu_{c-c(apom)}$), 1430 ($\nu_{c(apom)-p}$), 1375 (ν_{c-p}), 1332 (ν_{o-c-p}), 1280 (ν_{c-o}), 855 ($\delta_{c(apom)-h}$), 740-730 ($\delta_{c(apom)-h}$), 690 ($\delta_{c(apom)-h}$).

UV-spectrum: λ_{max} = 250q 340 nm

Example 2. $8,7.10^{-3}$ g of the catalyst (Example 1) and 20 cm^3 toluol are set in a metallic autoclave, supplied with a magnetic stirrer. The reactor is connected to an ethylene-dosing device. After reaching the work pressure the reaction mixture is heated to 70°C. Polymerization is carried on for 30 min. Yield of polyethylene: 6,8 g (Table 1).

Properties of Polyethylene Produced with catalyst 1

N of Example	Solvent	Concentr. Of Cat. x10^{4*} mol/l	P_{C2H4} at	$A_{cat.}$ kg/g Ni	M. w. of PE g/mol	M. p. of PE °C	Crystality of PE %	N of CH_3 per 1000 C-atoms	Density of PE kg/m^3
1	Toluol	3,3	20	8,81	281300	125,5	68,8	5,3	948
2	heptane	3,3	7	3,89	220700	124,0	68,0	5,8	945
3*	Cyclo-hexane	39	3,5	3,20					

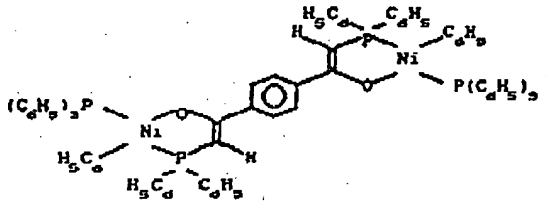
*The translator believes there is a printing mistake here and the correct writing out is **x10^{-4} mol/l.**

Reference data is taken from US 4 716 205

Example 3. 8,7.10^{-3} g catalyst (Example 1) and 20 cm^3 n-heptane are set in a metallic autoclave, supplied with a magnetic stirrer. The reactor is connected to an ethylene-dosing device. After reaching the work pressure the reaction mixture is heated to 70°C. Polymerization is carried on for 4 h. Yield of polyethylene: 3 g (Table 1).

PATENT CLAIMS

1. Catalyst for polymerization of ethylene of the following formula:



2. Method for producing a catalyst for polymerization of ethylene according to claim 1, characterized in that Ni (O) compounds react with bis-α-keto-ylides or with tertiary phosphines in a medium of polar or non-polar solvents, or mixtures thereof, at a temperature from -20°C to 80°C and reaction time from 30 min to 72 h.

3. The method according to claim 2, characterized in that bis-1,5-cyclo-octa-di-ene nickel (O), bis-nor-borna-di-ene nickel (O), tetra-cis-triphenyl-phosphine nickel (O), tetra-cis-trinaphtyl-phosphine nickel (O), are used as Ni (O) compounds.

4. The method according to claim 2, characterized in that ethers containing 3 to 20 carbon atoms, ketones containing 3 to 20 carbon atoms, esters containing 2 to 20 carbon atoms, tetrahydrofuran, dioxane, pyrridine, are used as polar solvents.

5. The method according to claim 2, characterized in that benzol, alkylaromatic hydrocarbons containing 7 to 20 carbon atoms, are used as non-polar solvents.

6. The method according to claim 2, characterized in that the catalyst is isolated from the reaction mixture by precipitation, filtration, evaporation of the solvent.

7. The method according to claim 6, characterized in that alkanes containing 5 to 20 carbon atoms, cycloalkanes containing 5 to 20 carbon atoms, are used for the precipitation of the catalyst.

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